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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: Yuasa, et al.

Serial No.: 10/787,222

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Title: POSITIVE ELECTRODE MATERIAL, ITS MANUFACTURING METHOD AND LITHIUM SECONDARY BATTERY

Art Unit: 1745

Examiner: Crepeau, J.

Conf. No.: 4833

DECLARATION UNDER 37 CFR 1.132

Commissioner for Patents
P. O. Box 1450
Alexandria, VA 22313-1450

Dear Sir:

I, Toyotaka Yuasa, declare as follows:

1. I am a citizen of Japan and am employed as a Senior Engineer by Hitachi Ltd., the headquarters of which is located at New Marunouchi Bldg. 5-1, Marunouchi 1-chome, Chiyoda-ku, Tokyo 100-8220, Japan. I graduated from Graduate School of Science and Technology of Tsukuba University, with a master's degree in 1989. I have been employed by Hitachi Ltd. since 1989 and have conducted research concerning "wiring of oxidation superconductors" from 1989 to 2001, and "positive electrode materials for lithium secondary batteries" from 2001 to 2009.

2. I am a co-inventor of the invention disclosed and claimed in the above-identified application.
3. I have read the office action mailed on March 10, 2009, and understand that the Examiner's position is that no clear difference in structure can be seen between the photos on "Sheet No. 1" and "Sheet No. 2" submitted with the Amendment and Submission Under 37 CFR 1.114 filed January 21, 2009 and attached hereto, except a difference in absolute particle size between both the primary particles and secondary particles.
4. I conducted measurements of primary particle sizes of the powders shown in "Sheet No. 1" and "Sheet No. 2" and obtained the result that the average primary particle size of the powder shown in "Sheet No. 1" is 0.2868 μm and the average primary particle size of the powders shown in "Sheet No. 2" is 0.6165 μm.
5. The following experiments were conducted by me or under my supervision to demonstrate that the sintering temperature difference of 70°C produces different products.
6. Experiments:
   a. Powdering and Mixture:
      i. Weighing: Nickel oxide, manganese oxide, and cobalt oxide were weighed to be a mole ratio of Ni: Mn: Co=33:33:33 and then were mixed.
      ii. Slurrying: Ion exchange water was added to the mixture so that the contents of powder in the slurry should become 10 -

30 wt %.

iii. Pulverization: The slurry and zirconia balls of 2 mm and 5 mm in diameter were introduced into a polyethylene pot, and then was subject to ball mill pulverization for 24 - 48 hours, at rotation of 1 Hz until the average diameter became approximately 0.5 μ m.

iv. Powdering: The slurry and zirconia beads of 0.3 - 0.5 mm in diameter were introduced into a media agitated type powdering machine to generate primary particles of 0.1-0.3μ m in diameter. Then, zirconia beads were removed from the slurry.

b. Granulation: The weight of raw powder in the slurry was measured based on specific gravity, and 0.1 - 1.0 wt% of polyvinyl alcohol (PVA) relative to raw powder was added as binder to the slurry. The slurry was dried by atomization by using a four fluid nozzle type atomizer to generate granulated particles.

c. Baking and Classification:

i. Baking: The granulated particles were introduced into a high purity alumina vessel, and were pre-baked at 500 - 600 °C for 10 hours to improve the bonding property between particles due to heat dissociation of PVA and baking. Then, lithium hydroxide and lithium carbonate were added to the pre-baked particles so that lithium contents became 1-1.1 mol with respect to transition metals. The powder mixture

was again introduced into the alumina vessel and main-baked at 900 °C for 10 hours to produce sample "A", and at 975 °C for 10 hours to produce sample "B".

ii. Classification: The samples of positive electrode material were classified with sieves of 22 - 24 μ m to remove large-sized particles.

d. Manufacturing of Test Electrode: The classified positive electrode material, carbon-containing conductive material, and 8 wt % of polyvinylidene fluoride dissolved in N-methyl-pyrrolidone (NMP) were mixed at weight ratio of 85: 10.7: 4.3. The mixture was applied on aluminum electric collector of 20μ m in thickness by using a blade coater having a gap of 100 μ m. Then it was dried at 80 °C for 1 hour and a disk of 15 mm in diameter was made by punch press. Further, it was dried at 120 °C for 3 hours under vacuum circumstances, and was pressed to be electrode density of 2.6 - 2.7 g/cm3 to produce a test positive electrode.

e. Estimation of charge/discharge properties by using Model Cell:

i. Manufacturing of Model Cell: The electric resistance was evaluated by using three pole type model cell configured similarly to electric battery. The test positive electrode as an electrode, aluminum electric collector, lithium metal as opposite electrode, and lithium metal as reference electrode were accumulated via separators immersed with electrolyte

and were pressed between a pair of stainless steel plates which were fixed with bolts under a predetermined torque. These plates were positioned in glass vessel to which electrolyte was added. In preparing the electrolyte, ethylene carbonate, dimethyl-carbonate, and diethyl-carbonate at volume ratio of 1:1:1 were mixed to make a solvent, to which lithium 6-fluoride phosphate was dissolved to 1 mol/l.

ii. Charge/Discharge Test: The charge/discharge properties of the model cell were evaluated by using a charge/discharge test machine. At first, the model cell was charged at constant electric current of 1.0 mA and constant electric voltage with upper limit voltage of 4.3 V for 6 hours as stop conditions. Then, the model cell was discharged 3 cycles at constant electric current of 1.0 mA and lower limit voltage of 3.0 V. Thus, the model cell was initialized. The initialized model cell was charged to 4.3 V, and then was cooled down to -30°C. The model cell was discharged at constant electric current of 2.1 mA and lower limit voltage of 3.0 V. As the results, the discharge capacity of "Sample A" was 4.5 mAh/g, and the discharge capacity of "Sample B" was 9.5 mAh/g.

f. Notes:

i. "Sample A" which was made at baking temperature of 900°C

for 10 hours corresponds to Comparative Example 1 disclosed in the specification.

ii. "Sample B" was made at baking temperature of 975°C for 10 hours and the discharge capacity of "Sample B" was 9.5 mAh/g at -30°C. On the other hand, Example 1 disclosed in the specification was made at baking temperature of 1000 °C for 3-10 hours and the discharge capacity of Example 1 was 10 mAh/g at -30°C. Comparing "Sample B" with Example 1, "Sample B" was made at lower baking temperature, and sintering was not fully completed. Therefore, the discharge capacity thereof was a little lower.

7. Based on the foregoing, I conclude that the sintering temperature difference of 70°C produces different products.

8. I declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Date 8/10/09

Signed: Toyotaka Yuasa
Toyotaka Yuasa